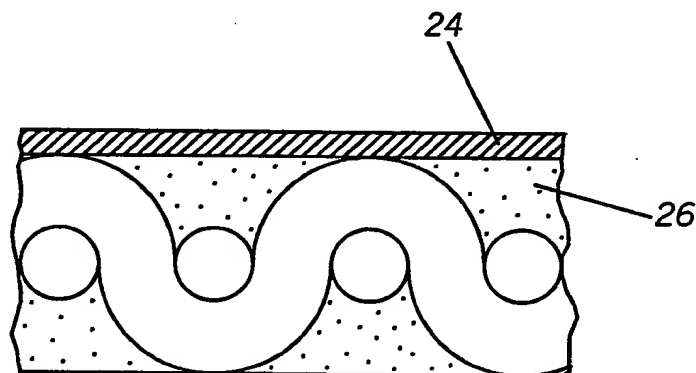




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : B32B 3/00, 5/16, 7/00 B32B 17/02	A1	(11) International Publication Number: WO 93/24314 (43) International Publication Date: 9 December 1993 (09.12.93)
(21) International Application Number: PCT/US93/04820 (22) International Filing Date: 20 May 1993 (20.05.93) (30) Priority data: 891,128 1 June 1992 (01.06.92) US (71) Applicant: MOTOROLA, INC. [US/US]; 1303 East Algonquin Road, Schaumburg, IL 60196 (US). (72) Inventors: PAPAGEORGE, Marc, V. ; 398 S.W. 13 Street, Boca Raton, FL 33486 (US). JUSKEY, Frank, J. ; 4103 N.W. 69 Terrace, Coral Springs, FL 33065 (US). NOU-NOU, Fadia ; 1321 N.W. 70 Avenue, Plantation, FL 33313 (US).		(74) Agents: DORINSKI, Dale, W. et al.; Motorola, Inc., Patent Dept., 8000 West Sunrise Boulevard, Fort Lauderdale, FL 33322 (US). (81) Designated States: JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>

(54) Title: THERMALLY CONDUCTIVE PRINTED CIRCUIT BOARD**(57) Abstract**

A thermally conductive circuit carrying substrate (29) is made from a layer of metal (24), a reinforcing medium (12), thermally conductive particles (15), and a resin (16). The resin has the thermally conductive particles dispersed throughout. The reinforcing medium and the resin-particle mixture are formed into a sheet-like laminated structure (19). The layer of metal is laminated to at least one side of the laminated structure to form a printed circuit board. The reinforcing medium is typically chopped or woven glass fibers, or paper sheets such as ARAMID[®]. Epoxy, cyanate ester, or polyimide resins are used, and aluminum nitride particles are dispersed throughout. A sheet of copper is used as the metal in order to define a circuit pattern on the printed circuit board. Each of the layers are stacked one atop the other and laminated by heat and pressure to form a solid laminar structure that has improved thermal conductivity compared to conventional laminate structures.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea	NO	Norway
BF	Burkina Faso	GR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	IE	Ireland	PT	Portugal
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SK	Slovak Republic
CI	Côte d'Ivoire	LI	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	MC	Monaco	TC	Togo
DE	Germany	MG	Madagascar	UA	Ukraine
DK	Denmark	ML	Mali	US	United States of America
ES	Spain	MN	Mongolia	VN	Viet Nam
FI	Finland				

THERMALLY CONDUCTIVE PRINTED CIRCUIT BOARD**5 Technical Field**

This invention relates generally to substrates for electronic assemblies, and more specifically to thermally conductive printed circuit board materials.

10 Background

Printed wiring boards, also known as printed circuit boards, PCBs, or PWBs, provide a conductive wiring path, support for components, interconnection of components, and a heat sink to aid in the thermal management of the total assembled package. The methods
15 used in producing printed circuit boards are either subtractive, using etched foil, or additive, using plated-up circuitry. In either case, the circuitry is formed on an insulating substrate or laminate material.

Printed circuit board materials are chosen for their mechanical and electrical characteristics and, of course, their relative material costs
20 and fabrication costs. The designer selects the optimum substrate for the application by comparing the various material properties and costs. The substrate mechanical properties that have an important bearing on the printed circuit board assembly are: water absorption, coefficient of thermal expansion, maximum operating temperature, flexural
25 strength, impact strength, tensile strength, shear strength, and thermal conductivity. Dielectric materials for printed circuit boards are typically polyester, epoxy, or polyimide impregnated fiberglass mat or cloth, the most popular being epoxy and fiberglass. It has relatively good dimensional stability, minimizing the incidence of cracks in plated
30 through holes, and its availability in a prepreg stage at reasonable cost also makes it the most desirable type of material for multilayer construction. One drawback of the epoxy/fiberglass laminate is the poor thermal conductivity. Epoxy/fiberglass and most other printed circuit board laminates have a thermal conductivity of about 0.23 to 0.28
35 Watt/Meter °C.

Integrated circuits or amplifiers that generate large amounts of heat must be mounted in a manner that will effectively dissipate this heat. In an attempt to meet these ever increasing demands, novel

lamine structures are employed to improve the substrate thermal conductivity or ability to dissipate heat. One example of this is a metal composite based on low expansion metal alloys such as invar clad with copper on one or both sides. These laminated structures are expensive and difficult to manufacture, and thus are used only in very specialized situations. Where large amounts of heat must be dissipated, specialty materials such as high thermal conductivity ceramic substrates are typically used instead of printed circuit boards. Clearly, a need exists for a circuit board material that possesses high thermal conductivity and the ease of manufacture and low cost of conventional epoxy/fiberglass substrates.

Summary of the Invention

Briefly, according to the invention, a thermally conductive circuit carrying substrate is made from a layer of metal, a reinforcing medium, thermally conductive particles, and a resin. The resin has the thermally conductive particles dispersed throughout. The reinforcing medium and the resin-particle mixture are formed into a sheet-like laminated structure. The layer of metal is laminated to at least one side of the structure to form a circuit carrying substrate.

In another embodiment, a thermally conductive printed circuit board comprises a glass fabric saturated with a resin containing thermally conductive particles dispersed throughout. The saturated fabric forms a laminated sheet, with a copper film adhered to at least one side of the laminated sheet.

In still another embodiment, a thermally conductive printed circuit board comprises a laminated sheet made from: 1) a layer of copper, 2) a first layer of a cyanate ester resin admixture having aluminum nitride particles dispersed throughout, 3) a sheet of ARAMID® paper, and 4) a second layer of a cyanate ester resin admixture having aluminum nitride particles dispersed throughout. Each layer is stacked one on top of the other and laminated to the other by heat and pressure to form a solid laminar structure.

Brief Description of the Drawings

FIG. 1 is a cross-sectional view of the thermally conductive laminate in accordance with the present invention.

3

FIG. 2 is a cross-sectional view of a thermally conductive printed circuit board in accordance with the present invention.

FIG. 3 is a cross-sectional view of an alternate embodiment of a thermally conductive printed circuit board in accordance with the present invention.

FIG. 4 is a cross-sectional view of another embodiment of a thermally conductive printed circuit board in accordance with the present invention.

10 Detailed Description of the Preferred Embodiment

The fabrication of printed circuit board laminates is a complex process beginning with formulation of the base resin. Resins such as epoxy, phenolic, polyimide, Teflon, polystyrene, and polyethylene are often used. The laminate is created by impregnating the base resin into a reinforcing medium. The reinforcing medium is typically a glass cloth woven from fibers of glass yarn, but can also be chopped glass fibers, paper sheets such as ARAMID® or other materials, or a composite of these. The resin is blended with a curing agent or catalyst and other materials such as flame retardants, flow promoters, or other modifying resins. The liquid resin is then placed in a dip tank into which the glass cloth or reinforcing medium is immersed in order to coat and impregnate the cloth with the liquid resin. The coated reinforcing medium is squeezed between metering rolls to form a mat, leaving a measured amount of resin on the surface and in the voids of the medium. The wet mat then passes into a tunnel dryer to remove any volatiles and begins the reaction to cure the resin to a predetermined stage. After this point, the mat is cut into sheets called prepregs. Sheets of the prepregs are then stacked and laminated in a high temperature press in order to form the finished printed circuit board substrate. A sheet of metal foil, typically copper, is usually laminated onto the outer layer of prepreg to form a metal clad laminated structure.

The reader will appreciate that while all materials may be considered to be thermally conductive to some extent, as a practical matter, plastic resins and other insulators such as glass, wood, and paper are such poor thermal conductors that they are generally considered to be thermally non-conductive, or thermal insulators. The term 'thermally conductive' used herein to describe materials that have a thermal conductivity significantly higher than those materials

that are normally considered to be thermal insulators. Those skilled in the art are cognizant of the difference between materials classified as 'thermally conductive' and those that are described as 'thermal insulators.'

5 The thermal conductivity (TC) of epoxy resins is typically reported in the literature to be about 0.2 Watt/Meter°C. For comparison, glass has a thermal conductivity of about 1.1 Watt/Meter°C (note: higher values denote greater thermal conductivity). The thermal conductivity of aluminum nitride (AlN) is around 280 Watt/Meter°C. Aluminum
10 nitride has been used in monolithic sheets as a substrate for hybrid modules requiring high heat dissipation. However, these substrates are very fragile and costly to manufacture.

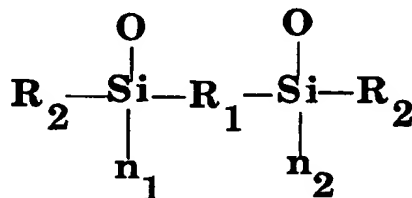
 Aluminum nitride can be obtained in particulate form and blended into resins to improve the thermal conductivity of the bulk resin.
15 However, as the oxygen content of AlN increases, the thermal conductivity decreases. The degradation in thermal conductivity due to oxygen content becomes significant when the surface to volume ratio of the AlN becomes large, as when particles are formed. Hence, the intrinsic thermal conductivity of AlN particles is not 280 Watt/Meter°C,
20 but around 85 Watt/Meter°C. By adding AlN particles to an epoxy resin, for example, improvements in the bulk thermal conductivity of the resin can be achieved. The TC of epoxy resins can be increased from the 0.2 Watt/Meter°C value for the neat resin, up to a value of 4 Watt/Meter°C for a volume loading of 62% AlN.

25 In one embodiment of the invention, particles of a highly thermally conductive material such as aluminum nitride, beryllium oxide, diamond, or silicon carbide in spherical or powder form are blended into the organic resin normally used in the production of a printed circuit board. Any of the conventional resins such as epoxy,
30 phenolic, polyimide, Teflon, polystyrene, and polyethylene may be used, but the user will find the greatest advantage by using high temperature resins such as polyimides or cyanate-esters. The newest class of resins to be developed for PCB applications are the carbon / silicone based polymers trade named SYCAR® from Hercules Chemical. These
35 resins are a new high performance thermosetting resin developed for printed circuit board applications. This new resin system combines excellent electrical properties and exceptional moisture resistance with conventional processability. This new class of resins has generated

5

great interest in applications where high speed / high frequency circuit boards are required, especially in adverse conditions such as high temperature and humidity. The structural formula of the carbon / silicone based polymers is:

5



After the appropriate amounts of the thermally conductive filler are dispersed in the resin, the circuit board is fabricated in a manner similar to that conventionally used. That is, the reinforcing medium is wet or impregnated with the resin/filler mixture and formed into a wet mat. The mat is then formed into a laminate with copper metal on at least one side in order to form a printed circuit substrate having high thermal conductivity. An illustrative example will now follow in order to elucidate the details.

15

EXAMPLE 1

A solvent, a resin, and AlN particles were blended to make a paste-like mixture.

20

Kerimid 601 polyimide resin	42.5% by weight
AlN particles	31.5% by weight
N-methyl pyrillidone	26.0% by weight

25

30

The polyimide resin was obtained from Rhône-Poulenc. The aluminum nitride was sintered grade, 30-50 micron size, spherical shaped particles, from Dow Chemical. A woven glass cloth was saturated with the above resin mixture, and the excess resin mixture was removed from the wet cloth to form a mat. The woven glass cloth was 2116 glass manufactured by Clark-Schwebel. The mat was baked at 125°C for one hour, then further cured by increasing the temperature from ambient to 300°C at 15°/minute, then held at 300°C for 5 minutes. The resulting laminate was approximately 33% woven glass cloth by weight.

CONTROL EXAMPLE 2

A control laminate was made in a manner similar to that of Example 1, but the AlN particles were omitted from the mixture.

5

Kerimid 601 polyimide resin	42.2% by weight
N-methyl pyrillidone	57.8% by weight

10

A woven glass cloth was saturated with the above resin solution, and the excess resin was removed from the wet cloth to form a mat. The mat was baked at 125°C for one hour, then further cured by increasing the temperature from ambient to 300°C at 15°/minute, then held at 300°C for 5 minutes. The glass cloth and resin were the same types as used in Example 1.

15

THERMAL CONDUCTIVITY MEASUREMENTS

The thermal conductivity of the laminates was measured in a differential scanning calorimeter (DuPont Instruments DSC 2100). Samples of each laminate were equilibrated at 30°C, and then ramped to 350°C at 15°/minute. The resulting DSC output revealed that the thermal conductivity of the laminate prepared in accordance with the invention (Example 1) was 1.64 Watt/Meter°C, whereas the thermal conductivity for the unfilled, control laminate was 1.52 Watt/Meter°C. Addition of the aluminum nitride to the laminate structure produced an eight percent improvement.

25

Referring now to FIG. 1, a cross sectional view of the laminate of Example 1, a woven glass cloth 10 consists of a network of glass fibers 12 interwoven in a pattern similar to that used to create cloth fabric. The individual fibers or bundles of fibers are woven to form a mesh, some fibers being perpendicular to the plane of the drawing and others being parallel to the plane of the drawing. Aluminum nitride particles 15 are dispersed throughout a resin matrix 16. The glass cloth 10 is saturated with the resin/AlN mixture, and the resulting mass is formed into a mat or sheet. Upon curing in a laminating press or other appropriate fixturing, the final laminated sheet-like structure 19 results.

35

Referring now to FIG. 2, a layer of metal 24 such as copper can also be added as a sheet or a foil to the laminated structure to form a laminate suitable for use as a printed circuit. The foil 24 is typically bonded to the laminate 29 by superimposing it upon the laminate prior to

final curing of the resin. This results in the foil 24 being firmly bonded to the resin 26. A second foil 37 may also be added to the other face or side of the laminate, to create a double sided printed circuit board as shown in FIG. 3. The second foil 37 is added at the same time as the first
5 foil 34, and the entire structure is cured up at the same time, thereby bonding both foils to the resin.

A laminated construction that is particularly useful as a high performance substrate is shown in FIG. 4. This system employs an ARAMID® paper reinforcing core 40. ARAMID® is used to provide
10 maximum control of the thermal coefficient of expansion of the laminate. Using the ARAMID® in paper form makes it easier to punch or drill the finished laminate, avoiding the problems normally found in using ARAMID® fiber reinforcements. The paper is coated with a
15 cyanate ester resin 46 containing aluminum nitride particles 45 in a manner similar to that outlined in the above examples, with the exception that when the paper is wet with the resin mixture, the resin does not saturate or impregnate into the interstices of the paper, but merely wets the surface. The resulting structure has the ARAMID®
20 paper 40 at the center of a sandwich comprising the aluminum nitride/resin mixture 48 on both sides. On at least one side, as foil of copper 44 is added, and the entire structure is cured up to form a high performance printed circuit board laminate.

The examples shown in FIGs. 1-4, while illustrative, are not meant to be considered limiting and other configurations of the
25 thermally conductive laminate may be envisioned and still fall within the spirit and scope of the invention. For example, multiple layers of prepregs could be used to create a thicker laminate. Additional layers of metal foil may be added, along with layers of prepreg, and a multilayer printed circuit board would result. Other types of resins or other types of
30 reinforcing mediums could be used, for example, a chopped glass core with outer layers having a woven glass mat. The aluminum nitride particles may be selectively placed in only the inner layers, only the outer layers, or in all the layers to custom tailor the thermal properties to the desires of the user.

35

What is claimed is:

Claims:

1. A thermally conductive, circuit carrying substrate,
comprising:
 - 5 a reinforcing medium;
a resin having particles of a thermally conductive material
dispersed throughout, the reinforcing medium and the
resin formed into a sheet having two major opposed
surfaces; and
 - 10 a layer of metal laminated to at least one major surface of the
sheet.
2. The thermally conductive, circuit carrying substrate of claim
1, wherein the resin is selected from the group consisting of epoxy,
15 polyimide, phenolic, polyester, cyanate ester, carbon / silicone, and
fluorinated polymers.
3. The thermally conductive, circuit carrying substrate of claim 1,
wherein the thermally conductive particles are selected from the group
20 consisting of aluminum nitride, beryllium oxide, aluminum oxide,
silicon carbide, diamond, and combinations thereof.
4. The thermally conductive, circuit carrying substrate of claim 3,
wherein the thermally conductive particles comprise between about 20
25 weight percent and about 70 weight percent of the resin.

5. A thermally conductive printed circuit board, comprising a laminated sheet of:

- 5 a woven glass fabric saturated with a resin, the resin having thermally conductive particles dispersed throughout; and
a copper film adhered to at least one side of the laminated sheet.

6. The thermally conductive printed circuit board of claim 5, wherein the thermally conductive particles are selected from the group consisting of aluminum nitride, beryllium oxide, aluminum oxide,
10 silicon carbide, diamond, and combinations thereof.

7. The thermally conductive printed circuit board of claim 6, wherein the thermally conductive particles comprise between about 20 weight percent and about 70 weight percent of the resin.
15

10

8. A thermally conductive printed circuit board laminate, comprising:

a laminated sheet having at least:

- 5 A) a first layer of copper;
 B) a first layer of a cyanate ester resin admixture having
 aluminum nitride particles dispersed throughout;
 C) a sheet of aramid paper; and
 D) a second layer of a cyanate ester resin admixture having
 aluminum nitride particles dispersed throughout;
10 and
 layers A, B, C, and D superposed in the order named, and
 laminated to each other by heat and pressure to form a solid
 laminar structure.

15 9. The thermally conductive printed circuit board of claim 8,
 further comprising a second layer of copper laminated to the laminated
 sheet on a side opposite to the side containing the first layer of copper.

20 10. The thermally conductive printed circuit board of claim 5,
 wherein the copper film is etched to form a circuitry pattern.

1/2

FIG.1

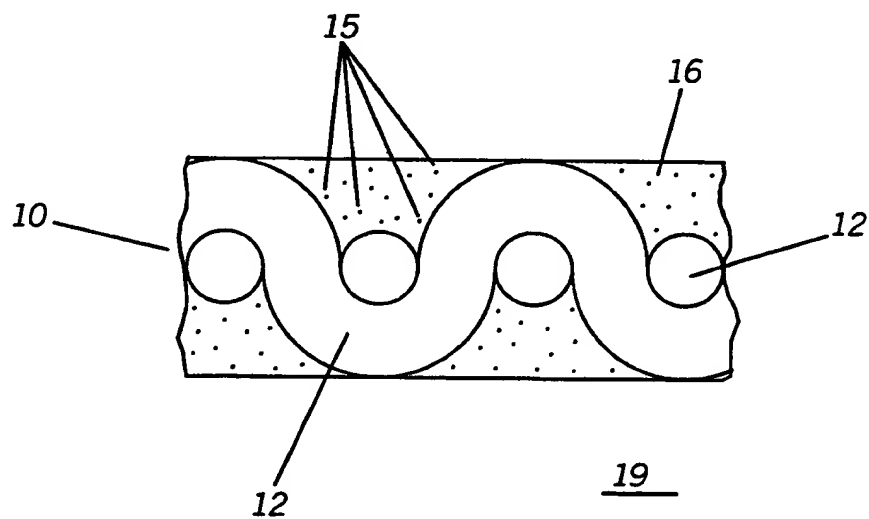
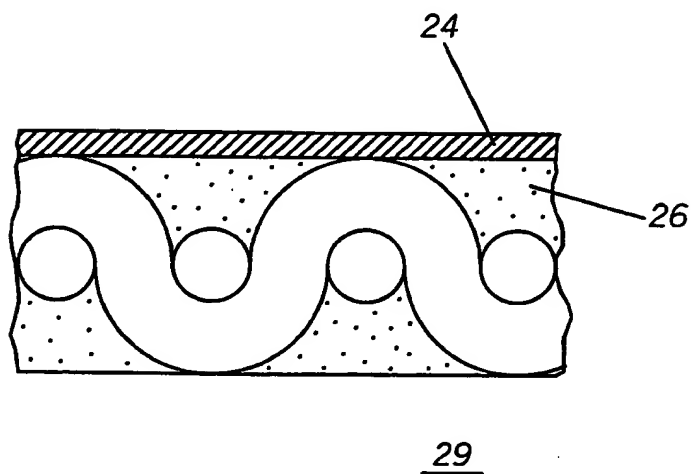


FIG.2



2/2

FIG. 3

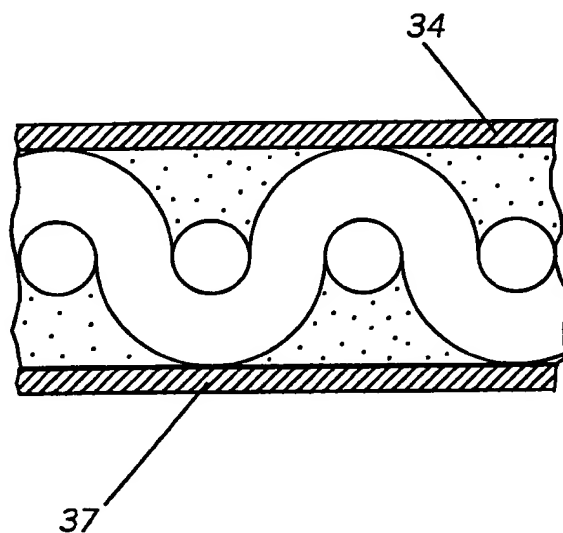
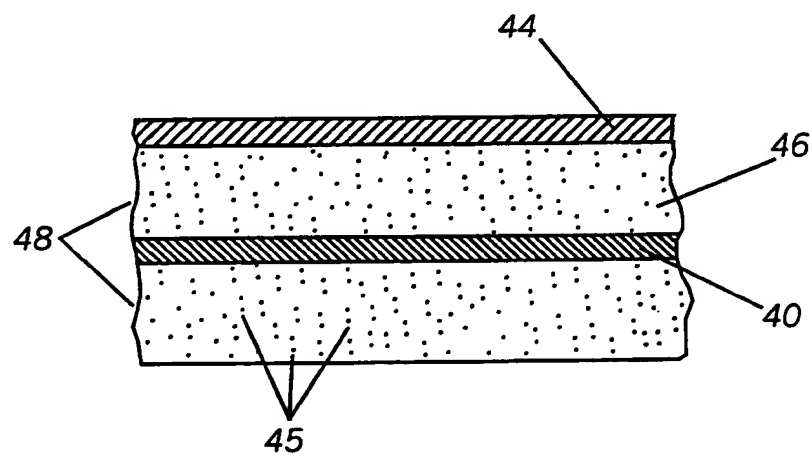


FIG. 4



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/04820

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :B32B 3/00, 5/16, 7/00, 17/02

US CL :428/195, 206, 209, 228, 240, 241, 268

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/195, 206, 209, 228, 240, 241, 268

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	GB, A, 2 060 435 (SHOWA DENKO KABUSHIKI) 07 MAY 1981, see entire document.	<u>1-7,10</u> 8,9
X Y	US, A, 4,869,954 (SQUITIERI) 26 SEPTEMBER 1989, see the Abstract.	<u>1-4</u> 5-10
Y	US, A, 4,770,922 (HATAKEYAMA et al) 13 SEPTEMBER 1988, see the Abstract.	1-10

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be part of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*g*	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

29 JUNE 1993

Date of mailing of the international search report

04 AUG 1993

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. NOT APPLICABLE

Authorized officer

ELIZABETH EVANS

Telephone No. (703) 308-2351

